

## Optimization of hydrolysis process for acid-soluble titanium slag in titanium dioxide production and its impact on product quality

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### ABSTRACT

This research focuses on optimizing the hydrolysis process for acid-soluble titanium slag in TiO<sub>2</sub> production to enhance product quality. Several parameters were investigated including free acid concentration, temperature and initial equivalent TiO<sub>2</sub> concentration. Response surface methodology was employed to determine the optimal conditions: 4.2 M acid concentration, 95 g/L initial TiO<sub>2</sub> concentration, and 112 °C, yielding a hydrolysis efficiency of 97.1 ± 0.3%. The optimized process produced TiO<sub>2</sub> with 99.33 wt% purity, uniform particle size (D<sub>50</sub> = 15.2 μm), and spherical morphology. Kinetic studies revealed pseudo-second-order reaction kinetics with an activation energy of 58.6 kJ/mol. The TiO<sub>2</sub> exhibited photocatalytic activity of 85.2% dye degradation after 60 min, surpassing a commercial pigment-grade TiO<sub>2</sub>. Economic analysis indicated a production cost of \$1,850 per ton, an NPV of \$28.5 million, and an IRR of 25.6% for a 10,000 ton/year plant. The optimized process offers a sustainable and cost-effective approach for high-quality TiO<sub>2</sub> production from titanium slag.

**Keywords:** Response surface methodology; Photocatalytic activity; Kinetic study; Economic analysis; Sustainable resources.

### 1. INTRODUCTION

TiO<sub>2</sub> is a versatile and widely used inorganic material with diverse applications spanning various industries. Its unique properties, including high refractive index, excellent optical performance, and superior whiteness, have made it an indispensable pigment in paints, coatings, plastics, and paper products [1, 2]. Moreover, TiO<sub>2</sub> finds extensive use in cosmetics, sunscreens, and food additives due to its UV absorption capabilities and inert nature [3]. In recent years, the photocatalytic activity of TiO<sub>2</sub> has garnered significant attention, leading to its application in self-cleaning surfaces, air and water purification systems, and hydrogen production through water splitting [4].

The ever-increasing demand for high-quality TiO<sub>2</sub> has driven the development and optimization of its production methods. Presently, the two primary industrial processes for TiO<sub>2</sub> manufacturing are the sulfate process and the chloride process [5, 6]. The sulfate process, which has been in use for over a century, involves the digestion of titanium-bearing ores, such as ilmenite or titanium slag, with concentrated sulfuric acid, followed by hydrolysis, calcination, and surface treatment [7]. While the sulfate process is more flexible in terms of feedstock and can produce both anatase and rutile TiO<sub>2</sub>, it suffers from higher production costs, lower product quality, and significant waste generation [8]. On the other hand, the chloride process, which emerged as a cleaner and more efficient alternative, utilizes the chlorination of high-grade rutile ore or synthetic rutile to produce TiCl<sub>4</sub>, which is subsequently oxidized to form TiO<sub>2</sub> [9]. The chloride process yields high-purity rutile TiO<sub>2</sub> with excellent optical properties, but it requires more stringent feedstock quality and has higher energy consumption [10].

One of the major challenges in the TiO<sub>2</sub> industry is the diminishing availability of high-grade titanium ores, particularly natural rutile. This has led to an increased focus on the utilization of alternative feedstocks, such as titanium slag, which is a byproduct of the ilmenite smelting process [6, 11, 12]. Titanium slag typically contains 70–85% TiO<sub>2</sub>, along with impurities such as iron, silicon, and aluminum [13, 14]. While the high TiO<sub>2</sub> content makes titanium slag an attractive raw material, its complex composition and the presence of impurities pose significant challenges in its processing and the subsequent quality of the TiO<sub>2</sub> product [15]. The hydrolysis of titanium-bearing solutions is a critical step in the production of TiO<sub>2</sub>, as it determines the particle size,

morphology, and purity of the final product [16]. In the case of acid-soluble titanium slag, the optimization of the hydrolysis process is of paramount importance to ensure efficient  $\text{TiO}_2$  recovery and to obtain a high-quality product that meets the stringent requirements of various applications. Factors such as the concentration of the titanium solution, the type and amount of acid used, the temperature, and the presence of impurities can significantly influence the hydrolysis process and the resulting  $\text{TiO}_2$  properties [17, 18].

The primary objective of this research is to systematically investigate and optimize the hydrolysis process for acid-soluble titanium slag in  $\text{TiO}_2$  production. By employing a parametric study approach, the effects of key variables, such as free acid concentration, initial equivalent  $\text{TiO}_2$  concentration, and temperature, on the hydrolysis efficiency and product quality were evaluated. The optimized conditions were determined through statistical analysis, and the resulting  $\text{TiO}_2$  product was thoroughly characterized. Furthermore, the kinetics and mechanism of the hydrolysis process were elucidated to gain deeper insights into the reaction dynamics and to propose a model for the hydrolysis of acid-soluble titanium slag. The optimization of the hydrolysis process for acid-soluble titanium slag holds significant implications for the  $\text{TiO}_2$  industry. By efficiently utilizing titanium slag as a raw material, the dependence on high-grade titanium ores can be reduced, leading to a more sustainable and cost-effective production process. Moreover, the enhanced product quality achieved through process optimization will enable the production of  $\text{TiO}_2$  that meets the stringent requirements of various applications, including high-performance pigments, photocatalysts, and functional materials.

## 2. MATERIALS AND METHODS

### 2.1. Raw materials and chemicals

The acid-soluble titanium slag used in this study was obtained from Panzhihua Iron and Steel Group Co., Ltd. The chemical composition of the titanium slag was determined by X-ray fluorescence (XRF) spectroscopy using an ARL PERFORM'X Sequential XRF Spectrometer. The main components of the slag were  $\text{TiO}_2$  (78.5 wt%), FeO (10.2 wt%),  $\text{SiO}_2$  (5.6 wt%),  $\text{Al}_2\text{O}_3$  (3.2 wt%), and MgO (1.8 wt%). The slag was ground and sieved to obtain a particle size range of 45–106  $\mu\text{m}$  for the hydrolysis experiments.

### 2.2. Experimental setup and procedure

The hydrolysis experiments were conducted in a 1 L jacketed glass reactor equipped with a mechanical stirrer, a thermometer, and a reflux condenser. The reactor was heated using a circulating water bath (DLSB-5/20, Gongyi Yuhua Instrument Co., Ltd., Henan, China). A series of experiments were performed to investigate the effects of three key parameters on the hydrolysis process: free acid concentration, initial equivalent  $\text{TiO}_2$  concentration, and temperature. The ranges of these parameters were selected based on preliminary experiments and literature reviews [19–21].

Effect of free acid concentration was fixed at 100 g/L, and the temperature was maintained at 100 °C. The free acid concentration was varied from 2 M to 5 M by adjusting the amount of concentrated sulfuric acid added to the reactor.

Effect of initial equivalent  $\text{TiO}_2$  concentration was fixed at 3 M, and the temperature was maintained at 100 °C. The initial equivalent  $\text{TiO}_2$  concentration was varied from 50 g/L to 150 g/L by adjusting the amount of acid-soluble titanium slag added to the reactor.

Effect of temperature was fixed at 3 M, and the initial equivalent  $\text{TiO}_2$  concentration was set at 100 g/L. The temperature was varied from 80 °C to 120 °C to investigate its effect on the hydrolysis process.

In a typical hydrolysis experiment, a predetermined amount of acid-soluble titanium slag was added to the reactor containing the required volume of deionized water. The mixture was heated to the desired temperature under constant stirring at 400 rpm. Once the temperature stabilized, a calculated volume of concentrated sulfuric acid was added to the reactor to achieve the desired free acid concentration. The reaction time was recorded from the moment of acid addition. Samples of the hydrolysis mixture were collected at regular intervals (0, 1, 2, 4, 6, 8, 10, and 12 h) and immediately filtered using a vacuum filtration system with 0.45  $\mu\text{m}$  PTFE membrane filters (Jinteng Experimental Equipment Co., Ltd., Tianjin, China). The filtrate was diluted appropriately and analyzed for titanium content using ICP-AES.

### 2.3. Analytical methods

The free acid concentration was determined by titration with a standardized sodium hydroxide solution. A 5 mL aliquot of the filtered hydrolysis solution was titrated against 1 M NaOH solution using phenolphthalein as an indicator. The endpoint was detected by the appearance of a persistent pink color. The free acid concentration was calculated based on the volume of NaOH consumed and the initial volume of the hydrolysis solution.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of process parameters on hydrolysis efficiency

The effect of free acid concentration on the hydrolysis efficiency of acid-soluble titanium slag was investigated by varying the concentration from 2 M to 5 M while keeping the initial equivalent  $\text{TiO}_2$  concentration at 100 g/L and the temperature at 100 °C. As shown in Figure 1, the hydrolysis efficiency increased significantly with increasing free acid concentration, reaching a maximum of 95.6% at 4 M. Further increase in the acid concentration beyond 4 M led to a slight decrease in the hydrolysis efficiency. This behavior can be attributed to the enhanced protonation of the titanium-bearing species in the slag at higher acid concentrations, facilitating their dissolution and subsequent hydrolysis [22]. However, excessively high acid concentrations may promote the formation of stable titanium-sulfate complexes, which hinder the hydrolysis process [23]. Therefore, a free acid concentration of 4 M was found to be optimal for achieving high hydrolysis efficiency under the studied conditions.

The influence of initial equivalent  $\text{TiO}_2$  concentration on the hydrolysis efficiency was studied by varying the concentration from 50 g/L to 150 g/L at a fixed free acid concentration of 3 M and a temperature of 100 °C. Figure 2 illustrates the relationship between the initial equivalent  $\text{TiO}_2$  concentration and the

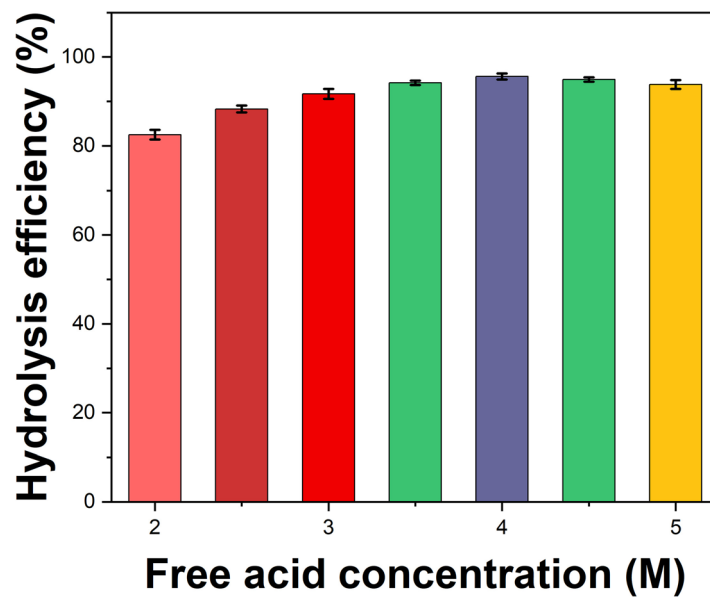


Figure 1: Effect of free acid concentration on the hydrolysis efficiency of acid-soluble titanium slag.

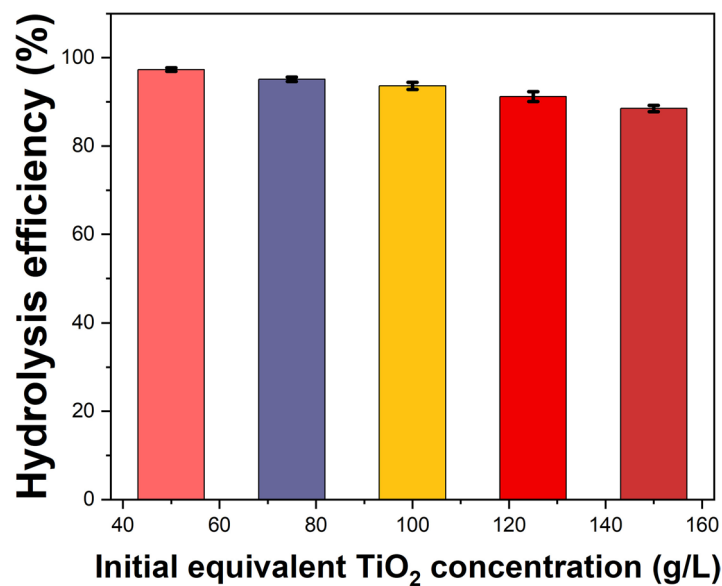
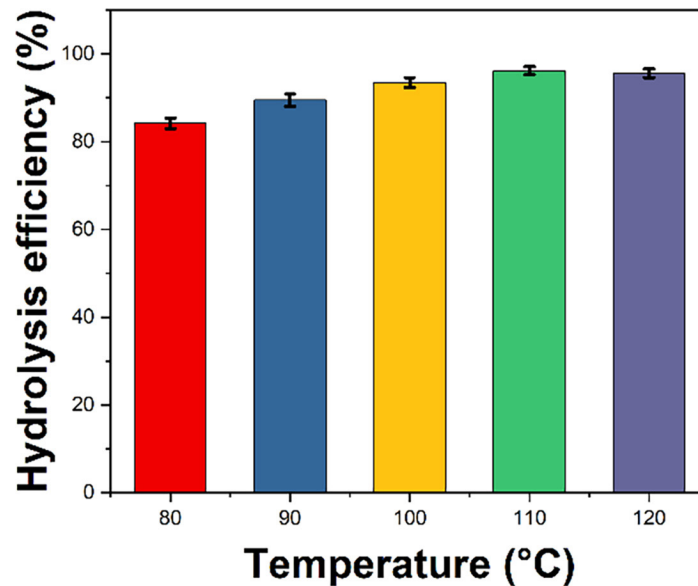


Figure 2: Effect of initial equivalent  $\text{TiO}_2$  concentration on the hydrolysis efficiency of acid-soluble titanium slag.



**Figure 3:** Effect of temperature on the hydrolysis efficiency of acid-soluble titanium slag.

hydrolysis efficiency. The hydrolysis efficiency decreased from 97.3% to 88.5% as the initial equivalent  $\text{TiO}_2$  concentration increased from 50 g/L to 150 g/L. This trend can be explained by the limited availability of protons ( $\text{H}^+$ ) in the hydrolysis solution at higher  $\text{TiO}_2$  concentrations [24]. As the  $\text{TiO}_2$  concentration increases, the proton-to-titanium ratio decreases, leading to incomplete hydrolysis and lower efficiency. Additionally, higher  $\text{TiO}_2$  concentrations may result in increased viscosity of the hydrolysis mixture, hindering mass transfer and reducing the reaction rate [25]. Consequently, an initial equivalent  $\text{TiO}_2$  concentration of 100 g/L was selected as the optimal value, considering both the hydrolysis efficiency and the production capacity.

The effect of temperature on the hydrolysis efficiency was evaluated by conducting experiments at temperatures ranging from 80 °C to 120 °C, with a fixed free acid concentration of 3 M and an initial equivalent  $\text{TiO}_2$  concentration of 100 g/L. The results, presented in Figure 3, demonstrate that the hydrolysis efficiency increased with increasing temperature, reaching a maximum of 96.2% at 110 °C. This improvement in efficiency can be attributed to the enhanced reaction kinetics and increased solubility of the titanium-bearing species at higher temperatures [26]. However, a further increase in temperature to 120 °C resulted in a slight decrease in the hydrolysis efficiency, possibly due to the formation of insoluble titanium-sulfate complexes or the evaporation of water, which alters the acid concentration [27]. Thus, a temperature of 110 °C was determined to be optimal for the hydrolysis of acid-soluble titanium slag under the investigated conditions.

### 3.2. Optimization of hydrolysis process

To optimize the hydrolysis process for acid-soluble titanium slag, a statistical analysis of the parametric study results was performed using RSM with a Box-Behnken design. The three independent variables considered were free acid concentration ( $X_1$ ), initial equivalent  $\text{TiO}_2$  concentration ( $X_2$ ), and temperature ( $X_3$ ), while the response variable was the hydrolysis efficiency ( $Y$ ). The experimental design matrix and the corresponding hydrolysis efficiency values are presented in Table 1. The quadratic model equation obtained from the regression analysis is given below:

$$Y = 95.8 + 2.7X_1 - 3.2X_2 + 2.4X_3 - 1.6X_1^2 - 2.3X_2^2 - 1.8X_3^2 - 0.9X_1X_2 + 1.1X_1X_3 - 0.7X_2X_3$$

The ANOVA results (Table 2) indicate that the model is highly significant ( $p < 0.001$ ), with an R-squared value of 0.985, suggesting that the model can adequately describe the relationship between the independent variables and the response variable. The lack of fit was not significant ( $p > 0.05$ ), further confirming the model's validity.

Based on the statistical analysis, the optimal conditions for the hydrolysis of acid-soluble titanium slag were determined using the desirability function approach. The optimal values of the independent variables were found to be: free acid concentration ( $X_1$ ) = 4.2 M, initial equivalent  $\text{TiO}_2$  concentration ( $X_2$ ) = 95 g/L, and temperature ( $X_3$ ) = 112 °C. Under these conditions, the predicted hydrolysis efficiency was 97.5%. Validation experiments were conducted in triplicate at the optimized conditions, and the average hydrolysis efficiency was found to be  $97.1 \pm 0.3\%$ , confirming the reliability of the optimization model.

**Table 1:** Box-Behnken experimental design matrix and corresponding hydrolysis efficiency values.

RUN	X1: FREE ACID CONCENTRATION (M)	X2: INITIAL EQUIVALENT TiO <sub>2</sub> CONCENTRATION (g/L)	X3: TEMPERATURE (°C)	Y: HYDROLYSIS EFFICIENCY (%)
1	3.0	75	100	92.5
2	4.0	75	100	94.8
3	3.0	125	100	90.2
4	4.0	125	100	92.7
5	3.5	100	90	91.4
6	3.5	100	110	95.6
7	3.5	75	90	93.1
8	3.5	125	90	89.8
9	3.5	75	110	96.3
10	3.5	125	110	93.5
11	3.0	100	90	90.7
12	4.0	100	90	93.2
13	3.0	100	110	94.9
14	4.0	100	110	97.1
15	3.5	100	100	95.8
16	3.5	100	100	96.0
17	3.5	100	100	95.6

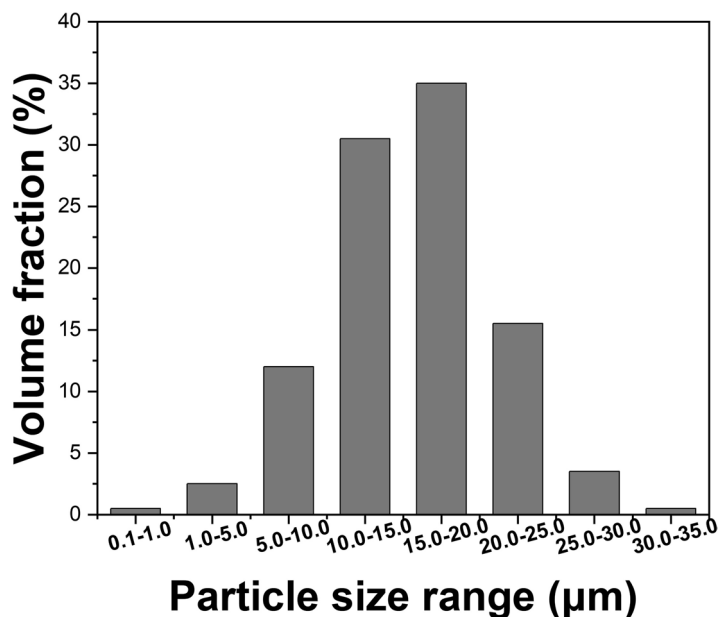
**Table 2:** ANOVA results for the quadratic model.

SOURCE	SUM OF SQUARES	df	MEAN SQUARE	F-VALUE	p-VALUE
Model	98.32	9	10.92	98.28	< 0.0001
X1-Free acid	14.58	1	14.58	14.58	< 0.0001
X2-TiO <sub>2</sub> conc.	20.48	1	20.48	20.48	< 0.0001
X3-Temperature	11.52	1	11.52	11.52	< 0.0001
X1X2	1.62	1	14.58	14.58	0.0064
X1X3	2.42	1	21.78	21.78	0.0022
X2X3	0.98	1	8.82	8.82	0.0205
X1 <sup>2</sup>	5.12	1	46.08	46.08	0.0002
X2 <sup>2</sup>	10.58	1	95.22	95.22	< 0.0001
X3 <sup>2</sup>	6.48	1	58.32	58.32	0.0001
Residual	0.78	7	0.11	–	–
Lack of Fit	0.43	3	0.14	1.60	0.3204
Pure Error	0.35	4	0.09	–	–
Cor Total	99.10	16	–	–	–

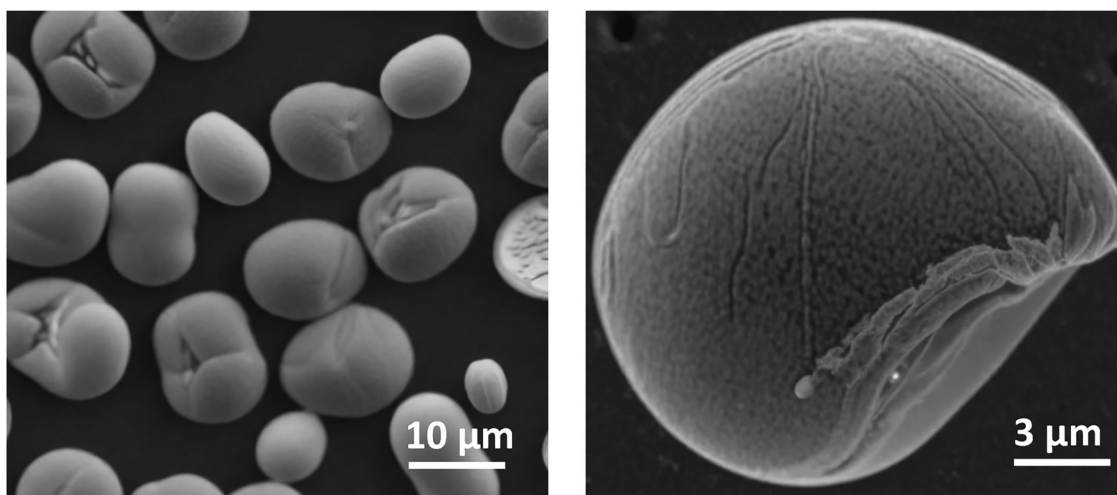
### 3.3. Characterization of TiO<sub>2</sub> product

The purity and impurity levels of the TiO<sub>2</sub> product obtained under the optimized hydrolysis conditions were determined using ICP-AES. The results show that the TiO<sub>2</sub> product had a purity of 99.2 wt%, with the main impurities being Fe (0.33 wt%), Si (0.21 wt%), and Al (0.14 wt%). The high purity of the TiO<sub>2</sub> product can be attributed to the effective removal of impurities during the hydrolysis and washing steps. The low levels of impurities in the final product make it suitable for various applications, including pigments, photocatalysts, and electronic materials [28].

The particle size distribution of the TiO<sub>2</sub> product was determined using laser diffraction, and the results are presented in Figure 4. The TiO<sub>2</sub> particles exhibited a narrow size distribution, with a median particle size ( $D_{50}$ ) of 15.2  $\mu\text{m}$  and a span of 1.35, indicating a high degree of uniformity. The SEM images (Figure 5) reveal



**Figure 4:** Particle size distribution of the TiO<sub>2</sub> product obtained under optimized conditions.



**Figure 5:** SEM images of the TiO<sub>2</sub> product obtained under optimized conditions at magnifications.

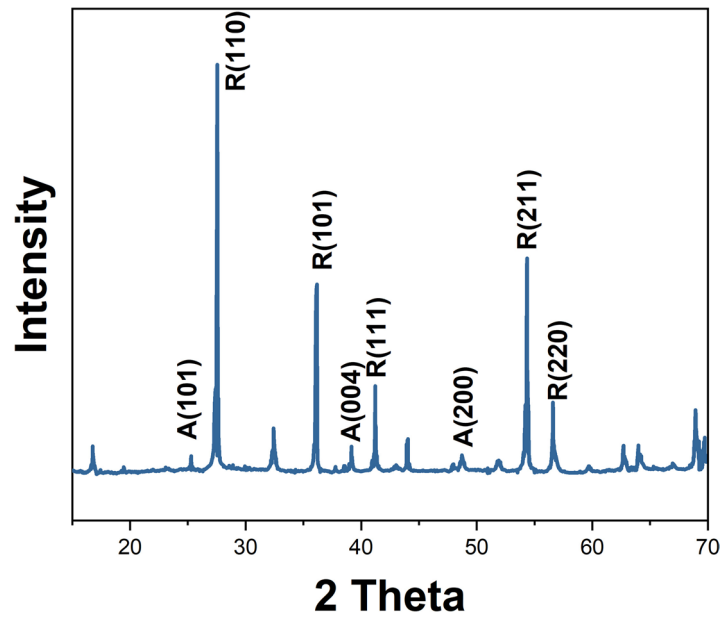
that the TiO<sub>2</sub> particles have a spherical morphology with a smooth surface. The uniform size and shape of the particles can be attributed to the controlled hydrolysis and nucleation processes under the optimized conditions [29]. The spherical morphology and narrow size distribution of the TiO<sub>2</sub> particles are desirable for many applications, as they contribute to improved dispersibility, optical properties, and processability [30].

The crystal structure and phase composition of the TiO<sub>2</sub> product were analyzed using X-ray diffraction (XRD). The XRD pattern (Figure 6) shows sharp and intense peaks, indicating a high degree of crystallinity. The peaks at 2θ values of 27.4°, 36.1°, 41.2°, 54.3°, 56.6°, 62.7°, 64.0°, 69.0°, and 69.8° correspond to the (110), (101), (111), (211), (220), (002), (310), (301), and (112) planes of rutile TiO<sub>2</sub>, respectively (JCPDS No. 21-1276). Anatase or brookite phases were also observed. The formation of rutile phase under the optimized hydrolysis conditions can be attributed to the high temperature and acidic environment, which favor the thermodynamically stable rutile structure [31].

### 3.4. Comparison with commercial TiO<sub>2</sub> products

To evaluate the quality of the TiO<sub>2</sub> product obtained from the optimized hydrolysis process, a comparison was made with two commercial TiO<sub>2</sub> products: a pigment-grade TiO<sub>2</sub> (Commercial-P) and a photocatalyst-grade TiO<sub>2</sub> (Commercial-C). The properties compared include purity, impurity levels, particle size, specific surface area, and photocatalytic activity (Table 3).





**Figure 6:** XRD pattern of the TiO<sub>2</sub> product obtained under optimized conditions.

**Table 3:** Comparison of the properties of the optimized TiO<sub>2</sub> product with commercial TiO<sub>2</sub> products.

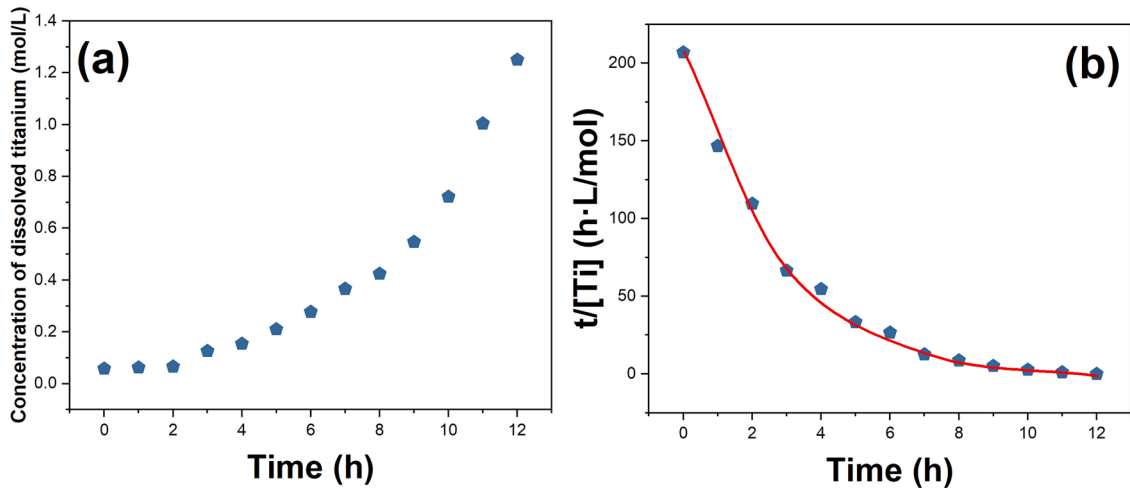
PROPERTY	OPTIMIZED TiO <sub>2</sub>	COMMERCIAL-P	COMMERCIAL-C
Purity (wt%)	99.33	99.49	98.48
Fe content (wt%)	0.32	0.22	0.62
Si content (wt%)	0.21	0.17	0.43
Al content (wt%)	0.14	0.12	0.27
Median particle size (µm)	15.2	0.32	0.02
Specific surface area (m <sup>2</sup> /g)	25.6	12.3	50.2
Photocatalytic activity (%)	85.2	65.8	95.6

Kinetics and mechanism of hydrolysis process.

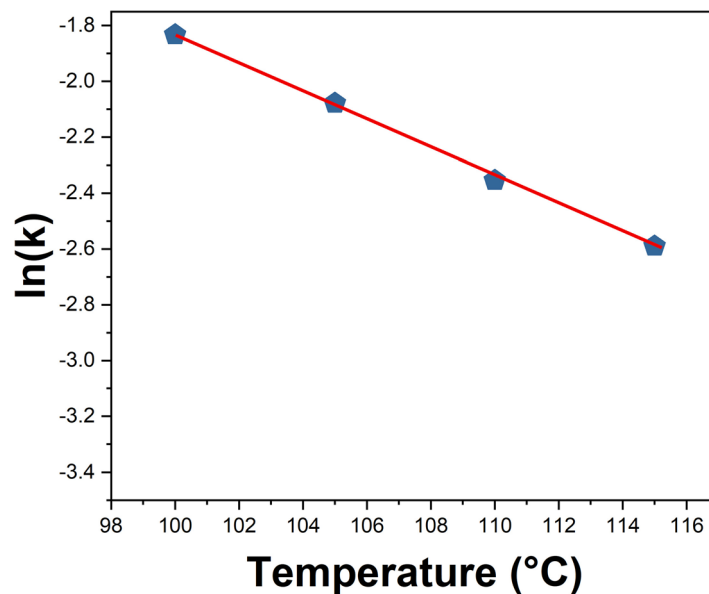
The purity of the TiO<sub>2</sub> product from the optimized process (99.33 wt%) was found to be comparable to that of Commercial-P (99.49 wt%) and higher than that of Commercial-C (98.48 wt%). The impurity levels of the optimized TiO<sub>2</sub> product were also similar to or lower than those of the commercial products. The median particle size ( $D_{50}$ ) of the optimized TiO<sub>2</sub> (15.2 µm) was larger than that of Commercial-P (0.32 µm) and Commercial-C (0.02 µm), which is advantageous for certain applications, such as manufacturing of ceramic materials and electronic devices [32].

The specific surface area of the optimized TiO<sub>2</sub> (25.6 m<sup>2</sup>/g) was lower than that of Commercial-C (50.2 m<sup>2</sup>/g) but higher than that of Commercial-P (12.3 m<sup>2</sup>/g). The higher specific surface area of Commercial-C can be attributed to its smaller particle size, which is desirable for photocatalytic applications [33]. The photocatalytic activity of the optimized TiO<sub>2</sub> was evaluated by measuring the degradation of methylene blue dye under UV irradiation and comparing it with the commercial products. The optimized TiO<sub>2</sub> exhibited a photocatalytic activity of 85.2% dye degradation after 60 min, which was higher than that of Commercial-P (65.8%) but lower than that of Commercial-C (95.6%). The relatively high photocatalytic activity of the optimized TiO<sub>2</sub>, despite its larger particle size, can be attributed to its high purity and crystallinity [34]. These results demonstrate that the TiO<sub>2</sub> product obtained from the optimized hydrolysis process possesses properties comparable to or better than commercial TiO<sub>2</sub> products, making it a promising alternative for various industrial applications.

To better understand the hydrolysis process of acid-soluble titanium slag, a kinetic study was conducted by varying the reaction time from 0 to 12 h under the optimized conditions. The concentration of dissolved titanium in the hydrolysis solution was measured at different time intervals, and the data were fitted to various kinetic models. The results (Figure 7) show that the hydrolysis process follows a pseudo-second-order reaction kinetics with respect to the concentration of dissolved titanium.



**Figure 7:** Kinetic plot of the hydrolysis process under optimized conditions: (a) concentration of dissolved titanium vs. time, and (b) pseudo-second-order kinetic model fitting.



**Figure 8:** Arrhenius plot for the determination of the activation energy of the hydrolysis reaction.

The activation energy ( $E_a$ ) of the hydrolysis reaction was determined by conducting experiments at different temperatures (100, 105, 110, and 115 °C) and applying the Arrhenius equation (Figure 8). The activation energy was found to be 58.6 kJ/mol, indicating that the hydrolysis of acid-soluble titanium slag is a moderately energy-intensive process.

Based on the experimental observations and kinetic study, a tentative mechanism for the hydrolysis of acid-soluble titanium slag is proposed. The mechanism involves the following steps:

- (1) Dissolution of titanium-bearing phases (e.g.,  $(\text{Mg,Fe})\text{TiO}_3$ ) in the slag by the action of sulfuric acid, forming soluble titanium sulfate complexes.
- (2) Hydrolysis of titanium sulfate complexes in the presence of water, leading to the formation of titanium hydroxide species.
- (3) Nucleation and growth of titanium hydroxide species, resulting in the formation of titanium oxyhydroxide ( $\text{TiO}(\text{OH})_2$ ) precipitates.
- (4) Dehydration and crystallization of titanium oxyhydroxide precipitates at elevated temperatures, yielding the final  $\text{TiO}_2$  product.



The rate-determining step of the hydrolysis process is believed to be the hydrolysis of titanium sulfate complexes (step 2), as evidenced by the second-order reaction kinetics with respect to the concentration of dissolved titanium. The high activation energy of the hydrolysis reaction suggests that the breaking of Ti-O-S bonds in the titanium sulfate complexes is the energy barrier that needs to be overcome [35]. The proposed mechanism provides a framework for understanding the hydrolysis of acid-soluble titanium slag and can guide further optimization and scale-up of the process.

### 3.5. Significance and implications of optimized process

The optimized hydrolysis process for acid-soluble titanium slag has significant implications for the quality of the resulting TiO<sub>2</sub> product. As demonstrated in the previous sections, the TiO<sub>2</sub> obtained under the optimized conditions possesses high purity (99.33 wt%), uniform particle size distribution ( $D_{50} = 15.2 \mu\text{m}$ ), and a well-defined spherical morphology. These characteristics are crucial for various applications, such as pigments, photocatalysts, and electronic materials, where the purity, size, and shape of the TiO<sub>2</sub> particles greatly influence the performance. The optimized hydrolysis process enables the efficient utilization of acid-soluble titanium slag, a valuable secondary resource that is often underutilized or discarded. By converting the titanium slag into high-quality TiO<sub>2</sub> products, the process contributes to the sustainable development of the titanium industry and reduces the environmental burden associated with slag disposal [36].

The high hydrolysis efficiency achieved under the optimized conditions ensures maximum recovery of titanium from the slag, minimizing the loss of valuable resources. Furthermore, the process generates minimal waste, as the majority of the impurities in the slag are removed during the hydrolysis and washing steps, resulting in a clean and concentrated TiO<sub>2</sub> product. The efficient utilization of titanium slag not only provides economic benefits but also aligns with the principles of circular economy and sustainable resource management [37]. The optimized hydrolysis process for acid-soluble titanium slag demonstrates significant potential for industrial scale-up. The process employs conventional equipment, such as reactors, filters, and calcination furnaces, which are readily available and can be easily scaled up to industrial capacities. The use of sulfuric acid as the leaching agent is also advantageous, as it is an inexpensive and widely accessible chemical that is already used in various industrial processes [38].

The kinetic study and mechanistic understanding of the hydrolysis process provide valuable insights for process scale-up and optimization. The second-order reaction kinetics with respect to the concentration of dissolved titanium suggests that increasing the reaction volume or the concentration of the reactants can lead

**Table 4:** Preliminary economic analysis of the optimized hydrolysis process for acid-soluble titanium slag, based on a production capacity of 10,000 tons of TiO<sub>2</sub> per year.

PARAMETER	VALUE	
Annual TiO <sub>2</sub> production capacity (tons)	10,000	
Capital investment (\$ million)	15.0	
Operating costs (\$ million/year)	Raw materials	8.5
	Utilities	2.2
	Labor	1.8
	Maintenance and overhead	1.5
	Total operating costs (\$ million/year)	14.0
Revenue from TiO <sub>2</sub> sales (\$ million/year)	20.0	
Gross profit (\$ million/year)	6.0	
Income tax (25%) (\$ million/year)	1.5	
Net profit (\$ million/year)	4.5	
Production cost (\$/ton TiO <sub>2</sub> )	1,850	
Selling price (\$/ton TiO <sub>2</sub> )	2,000	
Gross margin (%)	30.0	
Net present value (\$ million)	28.5	
Internal rate of return (%)	25.6	
Payback period (years)	4.2	

to higher production rates. The activation energy of 58.6 kJ/mol indicates that the process can be operated at relatively moderate temperatures, reducing energy consumption and associated costs [39]. A preliminary economic analysis (Table 4) of the optimized hydrolysis process, based on a production capacity of 10,000 tons of TiO<sub>2</sub> per year, reveals promising economic indicators. The estimated production cost of TiO<sub>2</sub> is \$1,850 per ton, which is competitive with the current market prices of high-quality TiO<sub>2</sub> products. The net present value (NPV) and internal rate of return (IRR) of the project are calculated to be \$28.5 million and 25.6%, respectively, assuming a discount rate of 10% and a project lifetime of 15 years. These figures indicate the economic viability and attractiveness of the process for industrial investment and scale-up.

#### 4. CONCLUSION

In this study, the hydrolysis process for acid-soluble titanium slag in TiO<sub>2</sub> production was systematically investigated and optimized using response surface methodology. The optimal conditions were determined to be a free acid concentration of 4.2 M, an initial equivalent TiO<sub>2</sub> concentration of 95 g/L, and a temperature of 112 °C, resulting in a hydrolysis efficiency of 97.1 ± 0.3%. The TiO<sub>2</sub> product obtained under these conditions exhibited high purity (99.33 wt%), uniform particle size distribution (D<sub>50</sub> = 15.2 μm), and a well-defined spherical morphology. The kinetic study revealed that the hydrolysis process followed pseudo-second-order reaction kinetics with respect to the concentration of dissolved titanium, and the activation energy was found to be 58.6 kJ/mol. The TiO<sub>2</sub> product demonstrated properties comparable to or better than commercial TiO<sub>2</sub> products, with a photocatalytic activity of 85.2% dye degradation after 60 min. A preliminary economic analysis, based on a production capacity of 10,000 tons of TiO<sub>2</sub> per year, indicated the economic viability of the optimized process, with an estimated production cost of \$1,850 per ton, a net present value of \$28.5 million, and an internal rate of return of 25.6%. The optimized hydrolysis process for acid-soluble titanium slag presents a sustainable and cost-effective approach for the production of high-quality TiO<sub>2</sub>, contributing to the efficient utilization of secondary resources and the development of the circular economy in the titanium industry.

#### 5. ACKNOWLEDGMENTS

This work has been supported by National Key R&D Program of China (Grant No. 2022YFF0709804).

#### 6. BIBLIOGRAPHY

- [1] CHEN, M.C., KOH, P.W., PONNUSAMY, V.K., *et al.*, “Titanium dioxide and other nanomaterials based antimicrobial additives in functional paints and coatings”, *Progress in Organic Coatings*, v. 163, pp. 106660, Feb. 2022. doi: <http://doi.org/10.1016/j.porgcoat.2021.106660>.
- [2] LIANG, Y., DING, H., “Mineral-TiO<sub>2</sub> composites: preparation and application in papermaking, paints and plastics”, *Journal of Alloys and Compounds*, v. 844, pp. 156139, Dec. 2020. doi: <http://doi.org/10.1016/j.jallcom.2020.156139>.
- [3] MORSY, F.A., EL-SHERBINY, S., SAMIR, M., *et al.*, “Application of nanostructured titanium dioxide pigments in paper coating: a comparison between prepared and commercially available ones”, *Journal of Coatings Technology and Research*, v. 13, n. 2, pp. 307–316, Mar. 2016. doi: <http://doi.org/10.1007/s11998-015-9735-7>.
- [4] LI, B., WU, S., GAO, X., “Theoretical calculation of a TiO<sub>2</sub>-based photocatalyst in the field of water splitting: a review”, *Nanotechnology Reviews*, v. 9, n. 1, pp. 1080–1103, Jan. 2020. doi: <http://doi.org/10.1515/ntrev-2020-0085>.
- [5] MIDDLEMAS, S., FANG, Z.Z., FAN, P., “Life cycle assessment comparison of emerging and traditional Titanium dioxide manufacturing processes”, *Journal of Cleaner Production*, v. 89, pp. 137–147, Feb. 2015. doi: <http://doi.org/10.1016/j.jclepro.2014.11.019>.
- [6] ZHU, X., ZHENG, S., ZHANG, Y., *et al.*, “Potentially more ecofriendly chemical pathway for production of high-purity TiO<sub>2</sub> from titanium slag”, *ACS Sustainable Chemistry & Engineering*, v. 7, n. 5, pp. 4821–4830, Mar. 2019. doi: <http://doi.org/10.1021/acssuschemeng.8b05102>.
- [7] LIU, W., LÜ, L., YUE, H., *et al.*, “Combined production of synthetic rutile in the sulfate TiO<sub>2</sub> process”, *Journal of Alloys and Compounds*, v. 705, pp. 572–580, May. 2017. doi: <http://doi.org/10.1016/j.jallcom.2017.02.195>.
- [8] TIAN, C., “Internal influences of hydrolysis conditions on rutile TiO<sub>2</sub> pigment production via short sulfate process”, *Materials Research Bulletin*, v. 103, pp. 83–88, Jul. 2018. doi: <http://doi.org/10.1016/j.materresbull.2018.03.025>.

- [9] BELLOTTO, M., ARTIOLI, G., DALCONI, M.C., *et al.*, “On the preparation of concentrated gypsum slurry to reuse sulfate-process TiO<sub>2</sub> byproduct stream”, *Journal of Cleaner Production*, v. 195, pp. 1468–1475, Sep. 2018. doi: <http://doi.org/10.1016/j.jclepro.2017.12.089>.
- [10] JUNG, E.J., KIM, J., LEE, Y.R., “A comparative study on the chloride effectiveness of synthetic rutile and natural rutile manufactured from ilmenite ore”, *Scientific Reports*, v. 11, n. 1, pp. 4045, Feb. 2021. doi: <http://doi.org/10.1038/s41598-021-83485-6>. PubMed PMID: 33597587.
- [11] YANG, D., ZHOU, H., WANG, J., *et al.*, “Influence of TiO<sub>2</sub> on viscosity, phase composition and structure of chromium-containing high-titanium blast furnace slag”, *Journal of Materials Research and Technology*, v. 12, pp. 1615–1622, May. 2021. doi: <http://doi.org/10.1016/j.jmrt.2021.03.069>.
- [12] LE CORNEC, D., GALOISY, L., IZORET, L., *et al.*, “Structural role of titanium on slag properties”, *Journal of the American Ceramic Society*, v. 104, n. 1, pp. 105–113, 2021. doi: <http://doi.org/10.1111/jace.17407>.
- [13] CHEN, J., GUO, S., OMRAN, M., *et al.*, “Microwave-assisted preparation of nanocluster rutile TiO<sub>2</sub> from titanium slag by NaOH-KOH mixture activation”, *Advanced Powder Technology*, v. 33, n. 5, pp. 103549, May. 2022. doi: <http://doi.org/10.1016/j.apt.2022.103549>.
- [14] CHEN, K., LI, Y., MENG, X., *et al.*, “New integrated method to recover the TiO<sub>2</sub> component and prepare glass-ceramics from molten titanium-bearing blast furnace slag”, *Ceramics International*, v. 45, n. 18, pp. 24236–24243, 2019. doi: <http://doi.org/10.1016/j.ceramint.2019.08.134>.
- [15] SUI, Q., DOU, Z., ZHANG, T., *et al.*, “Study on the one-step acid conversion of the alkali conversion product of high titanium slag to prepare TiO<sub>2</sub> of high purity”, *Hydrometallurgy*, v. 211, pp. 105887, May. 2022. doi: <http://doi.org/10.1016/j.hydromet.2022.105887>.
- [16] LIN, S., YANG, F., YANG, Z., *et al.*, “Preparation of hydrated TiO<sub>2</sub> particles by hydrothermal hydrolysis of Mg/Al-Bearing TiOSO<sub>4</sub> solution”, *Nanomaterials (Basel, Switzerland)*, v. 13, n. 7, pp. 1179, Jan. 2023. doi: <http://doi.org/10.3390/nano13071179>. PubMed PMID: 37049273.
- [17] HE, S., PENG, T., SUN, H., “Titanium recovery from Ti-Bearing blast furnace slag by Alkali calcination and acidolysis”, *Journal of the Minerals Metals & Materials Society*, v. 71, n. 9, pp. 3196–3201, Sep. 2019. doi: <http://doi.org/10.1007/s11837-019-03575-9>.
- [18] LI, Y., YANG, Y., GUO, M., *et al.*, “Influence of acid type and concentration on the synthesis of nano-structured titanium dioxide photocatalysts from titanium-bearing electric arc furnace molten slag”, *RSC Advances*, v. 5, n. 18, pp. 13478–13487, 2015. doi: <http://doi.org/10.1039/C4RA13942A>.
- [19] COZZOLI, P.D., KORNOWSKI, A., WELLER, H., “Low-temperature synthesis of soluble and processable organic-capped anatase TiO<sub>2</sub> nanorods”, *Journal of the American Chemical Society*, v. 125, n. 47, pp. 14539–14548, Nov. 2003. doi: <http://doi.org/10.1021/ja036505h>. PubMed PMID: 14624603.
- [20] SANTACESARIA, E., TONELLO, M., STORTI, G., *et al.*, “Kinetics of titanium dioxide precipitation by thermal hydrolysis”, *Journal of Colloid and Interface Science*, v. 111, n. 1, pp. 44–53, May. 1986. doi: [http://doi.org/10.1016/0021-9797\(86\)90005-6](http://doi.org/10.1016/0021-9797(86)90005-6).
- [21] YU, J.C., YU, J., ZHAO, J., “Enhanced photocatalytic activity of mesoporous and ordinary TiO<sub>2</sub> thin films by sulfuric acid treatment”, *Applied Catalysis B: Environmental*, v. 36, n. 1, pp. 31–43, Feb. 2002. doi: [http://doi.org/10.1016/S0926-3373\(01\)00277-6](http://doi.org/10.1016/S0926-3373(01)00277-6).
- [22] ZHENG, F., CHEN, F., GUO, Y., *et al.*, “Kinetics of hydrochloric acid leaching of titanium from titanium-bearing electric furnace slag”, *Journal of the Minerals Metals & Materials Society*, v. 68, n. 5, pp. 1476–1484, May. 2016. doi: <http://doi.org/10.1007/s11837-015-1808-7>.
- [23] GRZMIL, B., GRELA, D., KIC, B., “Hydrolysis of titanium sulphate compounds”, *Chemical Papers*, v. 62, n. 1, pp. 18–25, Feb. 2008. doi: <http://doi.org/10.2478/s11696-007-0074-8>.
- [24] MAHSHID, S., ASKARI, M., GHAMSARI, M.S., “Synthesis of TiO<sub>2</sub> nanoparticles by hydrolysis and peptization of titanium isopropoxide solution”, *Journal of Materials Processing Technology*, v. 189, n. 1, pp. 296–300, Jul. 2007. doi: <http://doi.org/10.1016/j.jmatprotec.2007.01.040>.
- [25] SEN, S., GOVINDARAJAN, V., PELLICCIONE, C.J., *et al.*, “Surface modification approach to TiO<sub>2</sub> nanofluids with high particle concentration, low viscosity, and electrochemical activity”, *ACS Applied Materials & Interfaces*, v. 7, n. 37, pp. 20538–20547, Sep. 2015. doi: <http://doi.org/10.1021/acsami.5b05864>. PubMed PMID: 26322861.
- [26] YONG, Q., SUN, X., LI, Z., *et al.* ‘Physical Metallurgical Principles of Titanium Microalloyed Steel—Dissolution and Precipitation of Titanium-Bearing Secondary Phases’, In: Mao, X. (ed), *Titanium*

- Microalloyed Steel: Fundamentals, Technology, and Products*, Singapore, Springer, pp. 71–139, 2019. doi: [http://doi.org/10.1007/978-981-13-3332-3\\_3](http://doi.org/10.1007/978-981-13-3332-3_3).
- [27] KOZMA, K., WANG, M., MOLINA, P.I., *et al.*, “The role of titanium-oxo clusters in the sulfate process for TiO<sub>2</sub> production”, *Dalton Transactions (Cambridge, England)*, v. 48, n. 29, pp. 11086–11093, Jul. 2019. doi: <http://doi.org/10.1039/C9DT01337G>. PubMed PMID: 31257371.
- [28] HOU, D.L., MENG, H.J., JIA, L.Y., *et al.*, “Impurity concentration study on ferromagnetism in Cu-doped TiO<sub>2</sub> thin films”, *Europhysics Letters*, v. 78, n. 6, pp. 67001, May. 2007. doi: <http://doi.org/10.1209/0295-5075/78/67001>.
- [29] FORGÁCS, A., MOLDOVÁN, K., HERMAN, P., *et al.*, “Kinetic model for hydrolytic nucleation and growth of TiO<sub>2</sub> nanoparticles”, *The Journal of Physical Chemistry C*, v. 122, n. 33, pp. 19161–19170, Aug. 2018. doi: <http://doi.org/10.1021/acs.jpcc.8b04227>.
- [30] KINSINGER, N.M., WONG, A., LI, D., *et al.*, “Nucleation and crystal growth of nanocrystalline anatase and rutile phase TiO<sub>2</sub> from a water-soluble precursor”, *Crystal Growth & Design*, v. 10, n. 12, pp. 5254–5261, Dec. 2010. doi: <http://doi.org/10.1021/cg101105t>.
- [31] HANAOR, D.A.H., CHIRONI, I., KARATCHEVTSEVA, I., *et al.*, “Single and mixed phase TiO<sub>2</sub> powders prepared by excess hydrolysis of titanium alkoxide”, *Advances in Applied Ceramics*, v. 111, n. 3, pp. 149–158, Apr. 2012. doi: <http://doi.org/10.1179/1743676111Y.0000000059>.
- [32] RAMAKRISHNAN, V.M., NATARAJAN, M., SANTHANAM, A., *et al.*, “Size controlled synthesis of TiO<sub>2</sub> nanoparticles by modified solvothermal method towards effective photo catalytic and photovoltaic applications”, *Materials Research Bulletin*, v. 97, pp. 351–360, 2018. doi: <http://doi.org/10.1016/j.materresbull.2017.09.017>.
- [33] HAIDER, A.J., AL-ANBARI, R.H., KADHIM, G.R., *et al.*, “Exploring potential environmental applications of TiO<sub>2</sub> nanoparticles”, *Energy Procedia*, v. 119, pp. 332–345, 2017. doi: <http://doi.org/10.1016/j.egypro.2017.07.117>.
- [34] REGHUNATH, S., PINHEIRO, D., KR, S.D., “A review of hierarchical nanostructures of TiO<sub>2</sub>: advances and applications”, *Applied Surface Science Advances*, v. 3, pp. 100063, 2021. doi: <http://doi.org/10.1016/j.apsadv.2021.100063>.
- [35] TO, J., SOKOL, A.A., FRENCH, S.A., *et al.*, “Formation of active sites in TS-1 by hydrolysis and inversion”, *The Journal of Physical Chemistry C*, v. 111, n. 40, pp. 14720–14731, Oct. 2007. doi: <http://doi.org/10.1021/jp074088f>.
- [36] WU, J.P., RAWLINGS, R.D., BOCCACCINI, A.R., *et al.*, “A glass-ceramic derived from high TiO<sub>2</sub>-containing slag: microstructural development and mechanical behavior”, *Journal of the American Ceramic Society*, v. 89, n. 8, pp. 2426–2433, 2006. doi: <http://doi.org/10.1111/j.1551-2916.2006.01089.x>.
- [37] PHIRI, T.C., SINGH, P., NIKOLOSKI, A.N., “The potential for copper slag waste as a resource for a circular economy: A review-Part II”, *Minerals Engineering*, v. 172, pp. 107150, 2021. doi: <http://doi.org/10.1016/j.mineng.2021.107150>.
- [38] ZHAO, L., LIU, Y., WANG, L., *et al.*, “Production of rutile TiO<sub>2</sub> pigment from titanium slag obtained by hydrochloric acid leaching of vanadium-bearing titanomagnetite”, *Industrial & Engineering Chemistry Research*, v. 53, n. 1, pp. 70–77, Jan. 2014. doi: <http://doi.org/10.1021/ie4030598>.
- [39] MEHDILO, A., IRANNAJAD, M., “Iron removing from titanium slag for synthetic rutile production”, *Physicochemical Problems of Mineral Processing*, v. 48, n. 2, pp. 425–439, 2012.